

Article

Ce_{1-x}Sn_xO₂ Catalysts Prepared with Combustion Method for Catalytic Combustion of Ethyl Acetate

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Abstract: A series of Ce_{1-x}Sn_xO₂ (X = 0, 0.2, 0.3, 0.4, 0.5, 0.9, 1) catalysts were synthesized via the combustion method. The physical and chemical structures of the prepared catalysts were systematically characterized by XRD, BET, SEM, TEM, XPS, and TPR. The Ce_{1-x}Sn_xO₂ catalysts have higher catalytic activities than the mono-oxide catalysts, as there are synergistic effects between CeO₂ and SnO₂. The catalytic activities of the Ce_{1-x}Sn_xO₂ catalysts are dependent on the X for the catalytic combustion of ethyl acetate (EA). The Ce_{1-x}Sn_xO₂ (X < 0.5) catalysts show high catalytic performances. Meanwhile, the Ce_{0.8}Sn_{0.2}O₂ and Ce_{0.7}Sn_{0.3}O₂ catalysts display the highest catalytic performance, with T₅₀ = 190 °C and T₉₀ = 210 °C. More importantly, the Ce_{0.8}Sn_{0.2}O₂ catalyst exhibits superior thermal and catalytic activity stability. It is found that the Ce_{1-x}Sn_xO₂ catalysts form solid solutions, as the X is < 0.5. The reduction of Sn⁴⁺ species to Sn²⁺ is significantly promoted by the CeO₂, which is an important factor attributed to the high catalytic activities of the solid solution Ce_{1-x}Sn_xO₂ catalysts. The catalytic activities of the Ce_{1-x}Sn_xO₂ catalysts exhibit a strong correlation to the surface atomic areas of Ce³⁺ and O_α (V_O). In other words, the higher surface atomic areas of Ce³⁺ and O_α (V_O) are, the higher the catalytic activities will have.

Keywords: VOCs; CeO₂-SnO₂ solid solution; oxygen vacancies



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1. Introduction

As one of the volatile organic compounds (VOCs), ethyl acetate (EA) is a precursor to tropospheric ozone and photochemical smog [1–4]. It mainly originates from industrial production, which poses a significant threat to human health and the environment [5]. Hence, the control and reduction of EA emissions have become increasingly imperative in recent years [3,6,7]. The implementation of end-of-pipe emission reduction technology has thus become prevalent to attain this objective. As the demand for sustainable production and environmental protection continues to grow, the adoption of these technologies is expected to increase in the future [5,7]. Due to its ability to efficiently eliminate harmful VOCs and minimize energy consumption, catalytic oxidation/combustion is widely regarded as an excellent treatment technology among various methods [8,9]. While VOC combustion catalysts play a pivotal role in catalytic combustion technology, their current performances fall short of the desired standards [2–4]. Therefore, the development of highly active catalysts is indispensable for enhancing the efficiency of catalytic combustion technology.

Significant progress has been achieved over the past decades in the development of catalysts for the catalytic combustion of VOCs. It has been shown that inexpensive non-noble metal oxides are viable alternatives to noble metal catalysts for the catalytic combustion of VOCs [10–14]. These oxides can always achieve high catalytic activities via improving their surface areas and redox activities, tuning surface chemistry properties [15,16]. Importantly, they possess better thermal stabilities and higher poisoning resistances, which

are crucial characteristics for long-term industrial applications. Notably, the CeO₂-based catalysts have been proven to be promising catalysts for oxidation reactions because of their excellent redox properties, which can even rival the performance of supported noble metal catalysts [17,18]. Due to the importance of the redox property to a highly active CeO₂-based catalyst, many attempts have been made to boost the ratio of Ce³⁺/Ce⁴⁺, enhancing the redox property of the catalyst and increasing the amount of oxygen vacancies (V_O) [17,19–23]. Usually, heteroatoms such as Zr [24–26], Ti [27,28], Mn [29–31] and Sn [32–37] were doped into CeO₂ lattice-forming solid solutions to increase their redox properties. Among them, the materials incorporating Sn into CeO₂ have been applied in various fields, including sensors [37], solid-state films [38], electrode materials [39,40], biological applications [40,41] and catalysts [33,36,42,43]. And the most interesting applications of CeO₂-SnO₂ were used for the environmental catalysts directly and catalyst supports [34–36,44–47]. Foletto et al. revealed that the CeO₂-SnO₂ nanocomposite with an optimum CeO₂ loading of 7 wt.% acted as an effective photocatalyst in the degradation of DB38 dye under sunlight [42]. Wang et al. demonstrated that Ce_{1-x}Sn_xO₂ composite oxide with a molar ratio of Sn:Ce = 4:6 exhibited the best catalytic performance for the soot oxidation reaction in the presence of water [36]. Jayachandran et al. found that the CeO₂-SnO₂/Al₂O₃ mixed oxides coated on the SS filter plates demonstrated a good catalytic performance in the exhaust emission test, which is a great challenge [48]. Zhou et al. reported that the CeSnO_x catalysts for the selective catalytic oxidation of NH₃ showed excellent N₂ selectivity at high temperatures compared to CeO₂ [44]. The Liu group reported that CeO₂-SnO₂ catalysts displayed high NH₃-SCR activity and with highly resisted the poisons of H₂O and SO₂ [45]. The addition of dopants of Sn⁴⁺ in the CeO₂ lattice increased the specific surface area and provided more V_O sites to enhance the adsorption of surface oxygen species, and then the catalytic performance and the thermal stability of SnO₂-CeO₂ were enhanced [33–36,45,48]. Although significant achievements have been made in the CeO₂-SnO₂ catalysts for varieties of catalytic reactions, Ce_{1-x}Sn_xO₂ catalysts for the catalytic combustion of VOCs has yet not to be fully explored.

In the present work, a series of Ce_{1-x}Sn_xO₂ composite oxide materials for the catalytic oxidation of EA were synthesized via a combustion approach. The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), H₂ temperature-programmed reduction (H₂-TPR), specific surface area determinations and X-ray photoelectron spectroscopy (XPS) to elucidate the structure–activity relationship.

2. Results and Discussion

2.1. XRD

The XRD patterns of the Ce_{1-x}Sn_xO₂ catalysts are displayed in Figure 1. It can be seen that the mono-oxides of SnO₂ and CeO₂ show a tetragonal crystalline phase (PDF No. 41-1445) and cubic fluorite phase (PDF No. 43-1002) [20,49,50]. The composite oxides of Ce_{1-x}Sn_xO₂ (X > 0.5) exhibit single SnO₂ phases of tetragonal crystalline. But the diffraction peak intensities of SnO₂ on the Ce_{0.1}Sn_{0.9}O₂ sample are weakened compared to those of the pure SnO₂. The crystalline size of SnO₂ is from 7.7 to 3.6 nm as the X decreases from 1.0 to 0.9, as shown in Table 1. Weak peaks at 26.788 and 51.730 two theta degrees attributed to the SnO₂ phase are about to disappear over the Ce_{0.5}Sn_{0.5}O₂ catalyst. The diffraction peaks of the SnO₂ phase disappear totally as the X is < 0.5, and the single phase of CeO₂ is observed. Furthermore, the positions of the diffraction peaks of CeO₂ shift to lower angles, from 29.282 to 28.622 two theta degree, accompanying the increase in the lattice parameters of CeO₂ from 5.2851 to 5.3806 Å (shown in Table 1) as the X decreases from 0.5 to 0.2. The above results indicate that the Sn⁴⁺ ions, with their radius diameters of 0.81 Å, which is smaller the radius diameters of of Ce⁴⁺ (0.97 Å) [20,51], enter the CeO₂ lattice and replace part of the Ce⁴⁺ ions to form a solid solution [52,53]. As a result of the solid solution formations, the CeO₂ crystalline sizes in the Ce_{1-x}Sn_xO₂ (0 < X ≤ 0.5) are smaller than those of the pristine CeO₂ (16.4 nm) shown in Table 1.

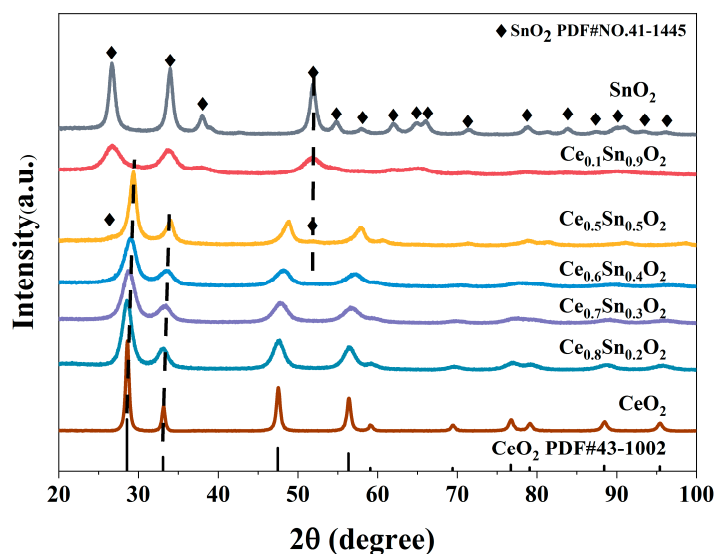


Figure 1. XRD patterns of the samples prepared by combustion methods.

Table 1. Crystalline sizes and lattice constants of the $Ce_{1-x}Sn_xO_2$ samples.

$Ce_{1-x}Sn_xO_2$	Crystalline Size (nm)		Lattice Constants (Å)	
	CeO ₂	SnO ₂	CeO ₂	SnO ₂
SnO ₂	/ *	7.7	/	4.7244
Ce _{0.1} Sn _{0.9} O ₂	/	3.6	/	4.7406
Ce _{0.5} Sn _{0.5} O ₂	7.6	/	5.2851	/
Ce _{0.6} Sn _{0.4} O ₂	5.4	/	5.3618	/
Ce _{0.7} Sn _{0.3} O ₂	4.2	/	5.3722	/
Ce _{0.8} Sn _{0.2} O ₂	5.4	/	5.3806	/
CeO ₂	16.4	/	5.3999	/

*: Not applicable.

2.2. SEM and BET Results

The SEM is one of the most popular tools used to characterize and analyze the morphology and surface of solid samples. Figure 2 displays the SEM images of the $Ce_{1-x}Sn_xO_2$ ($x = 0, 0.2, 0.4, 1$) catalysts. The SnO₂ catalyst presents a compact surface structure with no primary macropores. However, porous structures are clearly observed on the $Ce_{1-x}Sn_xO_2$ ($x = 0.2, 0.4$) catalysts shown in Figure 2b,c. And the CeO₂ morphology, with a notable reduction of macropores, lies between SnO₂ and $Ce_{1-x}Sn_xO_2$ (Figure 2d). The results show that the morphologies of $Ce_{1-x}Sn_xO_2$ show significant difference from the morphology of the pristine CeO₂ and SnO₂. Accordingly, the BET surface areas of $Ce_{1-x}Sn_xO_2$ listed in Table 2 are higher than those of the pure CeO₂. Among them, the Ce_{0.8}Sn_{0.2}O₂ and Ce_{0.1}Sn_{0.9}O₂ samples have the highest surface area (around 51 m²/g).

Table 2. BET surface areas, SAAs, and atomic proportions on the $Ce_{1-x}Sn_xO_2$ catalysts.

Catalyst	BET Surface Area (m ² /g)	Atomic Concentration (at%)					SAAs (m ² /g)	
		O		Ce		Sn	Ce ³⁺	O _α
		O _α	O _β	Ce ³⁺	Ce ⁴⁺			
CeO ₂	10.7	11.9	34.5	2.3	11.5	/ *	0.2	2.4
Ce _{0.8} Sn _{0.2} O ₂	51.4	15.1	35.8	2.3	9.6	3.9	1.1	13.4
Ce _{0.7} Sn _{0.3} O ₂	41.1	15.7	34.4	2.0	8.6	5.5	0.8	11.3
Ce _{0.6} Sn _{0.4} O ₂	37.3	15.5	34.9	2.2	7.7	7.2	0.7	10.0
Ce _{0.5} Sn _{0.5} O ₂	26.1	16.7	34.3	1.9	6.4	9.7	0.4	7.5
Ce _{0.1} Sn _{0.9} O ₂	51.6	8.6	41.8	0.7	2.0	17.8	0.3	7.6
SnO ₂	43.3	15.9	39.4	/	/	21.1	/	2.7

*: Not applicable.

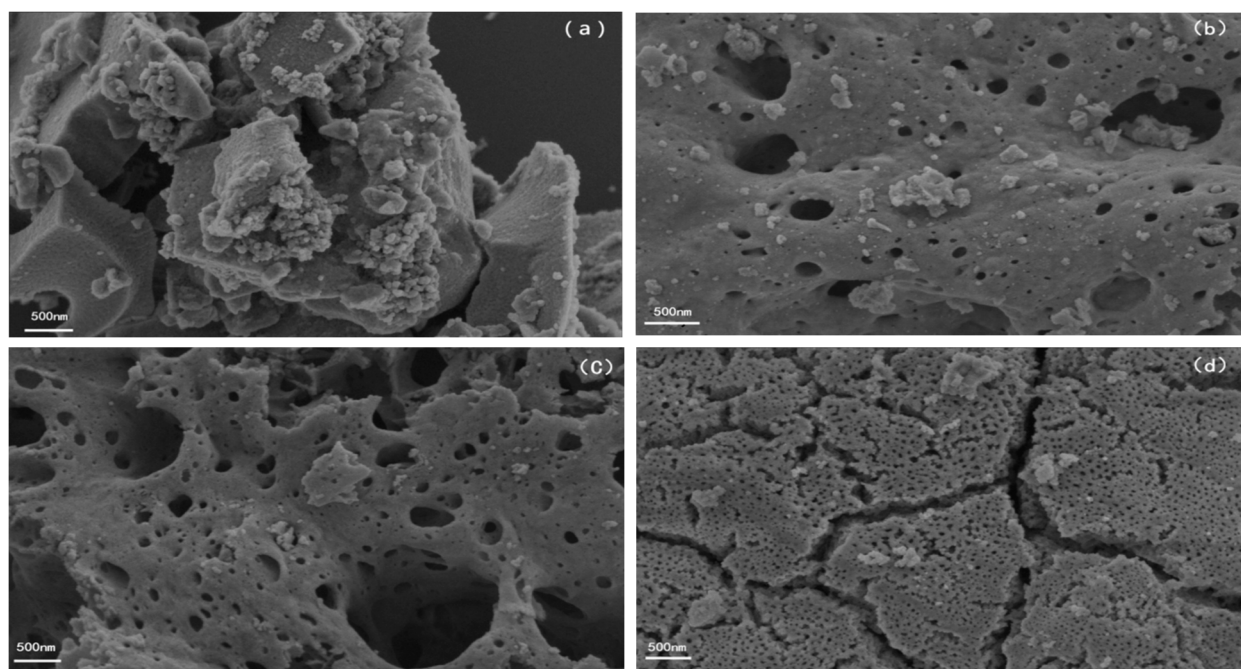


Figure 2. SEM images of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts: (a) SnO_2 , (b) $\text{Ce}_{0.6}\text{Sn}_{0.4}\text{O}_2$, (c) $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ and (d) CeO_2 .

SAAAs can be calculated by the following equations:

$$\text{SAAAs of Ce}^{3+} = \frac{\text{BET surface area}}{1 + \left(\frac{r_{\text{Ce}^{4+}}}{r_{\text{Ce}^{3+}}}\right)^2 \times \frac{C_{\text{Ce}^{4+}}}{C_{\text{Ce}^{3+}}} + \left(\frac{r_{\text{O}^{2-}}}{r_{\text{Ce}^{3+}}}\right)^2 \times \frac{C_{\text{O}^{2-}}}{C_{\text{Ce}^{3+}}} + \left(\frac{r_{\text{Sn}^{4+}}}{r_{\text{Ce}^{3+}}}\right)^2 \times \frac{C_{\text{Sn}^{4+}}}{C_{\text{Ce}^{3+}}}} \quad (1)$$

$$\text{SAAAs of O}^\alpha = \frac{\text{BET surface area}}{1 + \left(\frac{r_{\text{Ce}^{4+}}}{r_{\text{O}^{2-}}}\right)^2 \times \frac{C_{\text{Ce}^{4+}}}{C_{\text{O}^{2-}}} + \left(\frac{r_{\text{Ce}^{3+}}}{r_{\text{O}^{2-}}}\right)^2 \times \frac{C_{\text{Ce}^{3+}}}{C_{\text{O}^{2-}}} + \left(\frac{r_{\text{Sn}^{4+}}}{r_{\text{O}^{2-}}}\right)^2 \times \frac{C_{\text{Sn}^{4+}}}{C_{\text{O}^{2-}}}} \quad (2)$$

where $C_{\text{Ce}^{4+}}$, $C_{\text{Ce}^{3+}}$, $C_{\text{O}^{2-}}$ and $C_{\text{Sn}^{4+}}$ are the atomic concentrations of Ce^{4+} , Ce^{3+} , O^{2-} and Sn^{4+} , respectively. And $r_{\text{Ce}^{4+}}$, $r_{\text{Ce}^{3+}}$, $r_{\text{O}^{2-}}$, and $r_{\text{Sn}^{4+}}$ are 0.97, 1.02, 1.40 and 0.81 Å, respectively [51,53,54].

2.3. TEM Results

TEM is applied to deeply reveal information about the microstructure of a catalyst. The TEM image of CeO_2 in Figure 3a displays an interplanar spacing of 0.31 nm assigned to CeO_2 (111) lattice fringes [47,55,56]. As shown in Figure 3b, no SnO_2 crystal facets are observed over the $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ catalyst, and it is also proved by the XRD results that it has a single-phase fluorite structure. Nevertheless, crystal facets with d-spacing of 0.30 nm assigned to CeO_2 (111) lattice fringes are found [20,22]. The d-spacing value of CeO_2 over the $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ catalyst is slightly smaller than that of the pristine CeO_2 , indicating that the Sn atom is incorporated into the CeO_2 lattice to form a solid solution, as the radius of Sn (0.81 Å) is smaller than that of the Ce (0.97 Å). The prepared SnO_2 sample was also characterized by TEM, as shown in Figure 3c. The (111) and (101) planes of SnO_2 are recognized to have d-spacing values of 0.33 nm and 0.26 nm [22,50,57].

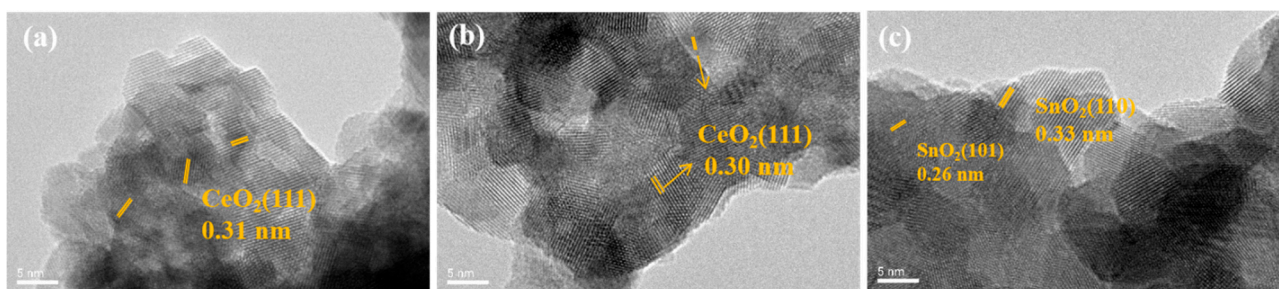


Figure 3. TEM images of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts: (a) CeO_2 , (b) $\text{Ce}_{0.8}\text{Sn}_{0.9}\text{O}_2$ and (c) SnO_2 .

2.4. H_2 -TPR Results

H_2 -TPR is a useful method to characterize the reduced property of a sample. The H_2 -TPR profiles of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts are presented in Figure 4. For the CeO_2 sample, it is well known that the peaks at ~ 500 (β) and >800 (γ_2) can be attributed to the reduction of the surface Ce^{4+} and bulk Ce^{4+} [58,59]. And the H_2 -TPR profile of SnO_2 shows two groups of reduction peaks with >450 (α) and ~ 670 (γ_1), which can be assigned to the reduction of surface of Sn^{4+} to Sn^{2+} and the reduction of bulk Sn^{4+} , along with the surface Sn^{2+} to metallic Sn [53]. However, the α peaks shift to a lower temperature, i.e., <350 $^\circ\text{C}$, over the $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ ($X = 0.2$ – 0.9), and this shift can be attributed to the reduction of the surface of Sn^{4+} to Sn^{2+} and the surface of Ce^{4+} to Ce^{3+} [51]. And the bulk CeO_2 peaks of γ_2 shift to lower temperatures at <800 $^\circ\text{C}$ as a result of the doping with Sn. Furthermore, the peak of γ_1 that emerged over the $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{O}_2$ can be assigned to the reduction of SnO_2 crystallites, as proved by the XRD result that weak diffraction peaks of SnO_2 appear on the $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{O}_2$. The reduction temperatures of the β peak increase from ~ 400 to 500 $^\circ\text{C}$ as the X increases from 0.2 to 0.9 , and these increases are tentatively ascribed to the reduction of Ce^{4+} and Sn^{4+} in the structures of Ce-O-Sn . The above results indicate that the reduction abilities of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts are promoted due to the promoted electron transfer between Ce and Sn species over the $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ [22,45,60].

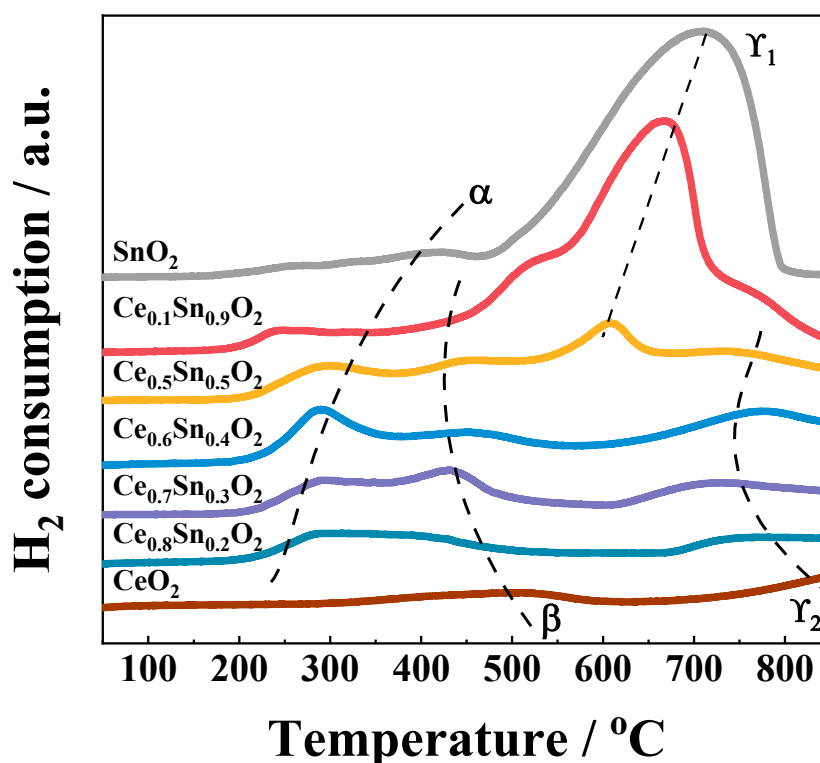


Figure 4. H_2 -TPR profiles of the $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts.

2.5. XPS Results

XPS was used to investigate the interactions among the metal oxides and the chemical states of oxygen, cerium and tin in the catalysts. As can be seen from Figure 5a, the O 1s bands can be deconvoluted into lattice oxygen (O_β) at 529.5–530.5 eV and adsorbed oxygen (O_α) at 531.5–532.5 eV [61,62]. Markedly, the binding energy of O_α shifts to a higher value, from 531.5 to 532.5 eV, when the X increases from 0 to 1 over the $Ce_{1-x}Sn_xO_2$ catalysts, indicating that the chemical state of O_α is changed as the CeO_2 is doped with the SnO_2 . The spectra of Ce 3d on the $Ce_{1-x}Sn_xO_2$ catalysts are shown in Figure 5b. According to the literature [60,62], the bands labeled with v^0 (~880.5 eV), v' (~884.7 eV) and u' (~903.2 eV) correspond to the Ce^{3+} , while the other bands are related to Ce^{4+} [24,32]. The spectrum of Sn 3d orbital shows two peaks at 495–494.7 and 486.3–486.6 eV, which are allocated to the Sn 3d_{3/2} and the Sn 3d_{5/2}, respectively [14,61]. Meanwhile, the Sn 3d_{5/2} and Sn 3d_{3/2} peaks of the $Ce_{1-x}Sn_xO_2$ (X = 0.2–0.9) shown in Figure 5c shift to low binding energy compared with that of SnO_2 , indicating that there are interactions between Ce and Sn in the $Ce_{1-x}Sn_xO_2$ catalysts. The results are consistent with the results of H_2 -TPR.

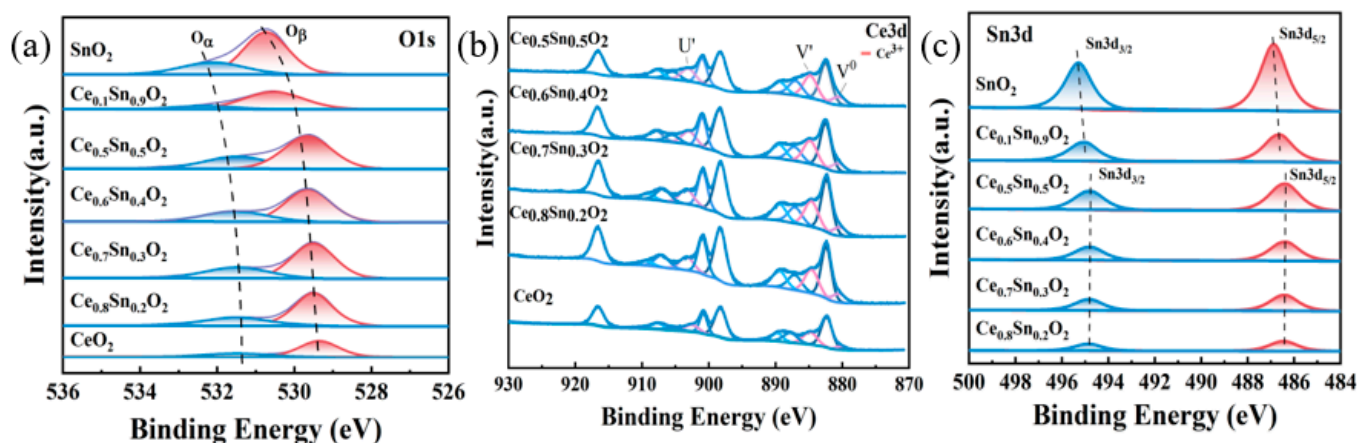


Figure 5. XPS spectra of the $Ce_{1-x}Sn_xO_2$ samples in the region of (a) O 1s, (b) Ce 3d and (c) Sn 3d.

And the atomic concentrations of Ce^{3+} , Ce^{4+} , O_α , O_β and Sn over the samples calculated from the XPS results are listed in Table 2. It is widely accepted that the catalytic oxidation activity is tightly correlated to the species of Ce^{3+} or O_α , which are derived from V_O [32,60,63]. Generally, the higher the concentrations of Ce^{3+} or O_α are, the higher the concentrations of the V_O present [10,54,64,65]. It is well known that the amount of V_O over a catalyst plays a crucial role in a catalytic oxidation reaction. The concentration of Ce^{3+} or O_α is used to characterize the amount of V_O on a catalyst, as it is difficult to accurately measure the concentration of V_O . However, it is not always satisfied to clarify the differences of catalytic activities over different catalysts through comparison with the surface atomic ratios of $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ and $O_\alpha/(O_\alpha + O_\beta)$ calculated by XPS results, because different catalysts always have different surface areas and Ce (Ce^{3+} and Ce^{4+}) concentrations. The surface atomic areas (SAAs) that are needed to achieve the authentic distribution of the Ce^{3+} or O_α species over the prepared catalysts are listed in Table 2, and they were calculated approximately based on the BET surface areas, their ionic radiuses and their surface atomic concentrations. It can be clearly seen that the SAAs of Ce^{3+} on the $Ce_{1-x}Sn_xO_2$ catalysts are higher than those of pure CeO_2 oxide. The SAAs of Ce^{3+} and O_α on the pure CeO_2 oxide are as low as 0.2 and 2.4. Moreover, the SAA of O_α on the pure SnO_2 oxide is 2.7. Nevertheless, the $Ce_{0.8}Sn_{0.2}O_2$ and $Ce_{0.7}Sn_{0.3}O_2$ catalysts possess high SAAs of Ce^{3+} (≥ 0.8 m²/g) and O_α (≥ 11.3 m²/g). It was revealed by the aforementioned XRD results that $Ce_{1-x}Sn_xO_2$ solid solutions are formed when the X is <0.5, indicating that the replacement of Ce^{4+} by Sn^{4+} in the CeO_2 lattice leads to the formation of a higher number of Ce^{3+} sites and a higher concentration of O_α , i.e., higher concentration of V_O [10,54,60,64].

2.6. Catalytic Activity

The effects of Sn on the $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts' catalytic activities are shown in Figure 6. Evidently, the catalytic activities of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ are heavily dependent on the X. The T_{50} and T_{90} over the SnO_2 catalyst are 280 °C and 300 °C. And the T_{50} and T_{90} over the CeO_2 catalyst are 225 °C and 250 °C. The activities of the pure mono-oxides of CeO_2 and SnO_2 are lower than those of the $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ ($X = 0, 0.2, 0.3, 0.4, 0.5, 0.9$) in the whole range of reaction temperatures (150–350 °C). The $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ and $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ catalysts show the highest catalytic activities with $T_{50} = 200$ °C and $T_{90} = 230$ °C. The catalytic activities are slightly decreased as the X increases to 0.4 and 0.5 on the $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts. Nevertheless, the catalytic performance is decreased significantly when the X is >0.5 on the $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$. The stability of the $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ catalyst was also tested at 210 °C, as shown in Figure 7. It is clearly shown that the $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ catalyst remains quite stable, maintaining an ~90% EA conversion during a 50 h time-on-stream reaction.

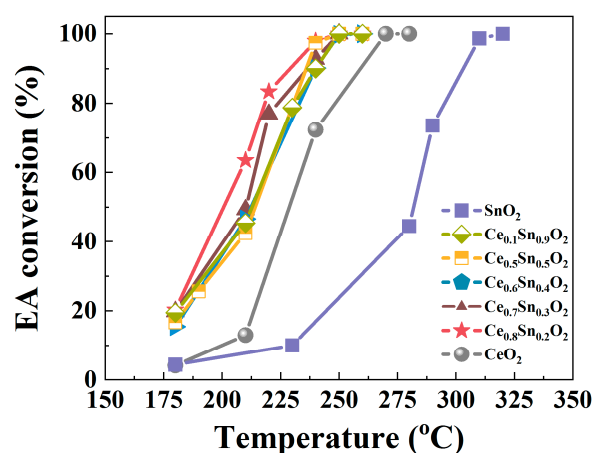


Figure 6. Catalytic activities of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts.

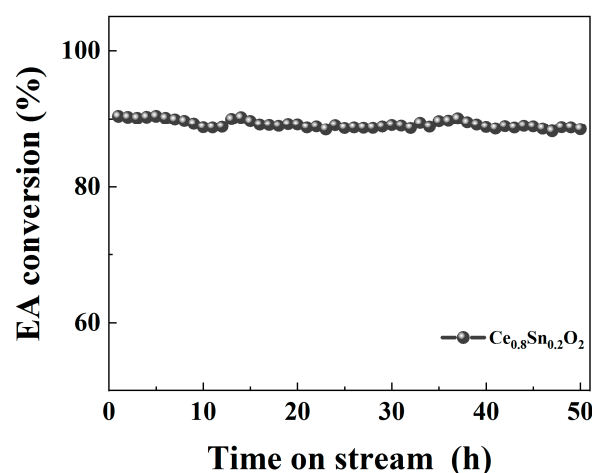


Figure 7. Stability of the $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ catalyst at 210 °C.

The catalytic performance results clearly indicate that there is a synergistic effect between SnO_2 and CeO_2 to promote the catalytic activities of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts. The H_2 -TPR results show that the reduction abilities of both Ce^{4+} and Sn^{4+} are promoted synergistically over the $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts. Especially, the reduction ability is significantly enhanced as the formation of the SnO_2 - CeO_2 solid solution, which means that it is easier to create the Ce^{3+} sites (V_O) from the Ce^{4+} by $2\text{Ce}^{4+} + \text{Sn}^{2+} \leftrightarrow 2\text{Ce}^{3+} + \text{Sn}^{4+}$ [36,45,53]. The high reduction abilities of the $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ solid solution catalysts may be responsible for their high activities. It is also found that the catalytic activities of the $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ catalysts

can strongly correlate to the SAA of Ce^{3+} and O_α (V_O) presented in Table 2. The solid solutions of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ ($x = 0.2, 0.3$) catalysts with the highest SAA of Ce^{3+} and O_α (V_O) have the best catalytic performances. And the pure mono-oxides of SnO_2 and CeO_2 with the lowest SAA of Ce^{3+} and O_α possess the poorest catalytic activities.

Thermal stability is one of the foremost concerns for industrial application of a VOC combustion catalyst. Therefore, the catalysts were subjected to calcination at 800 °C for 4 h to test their thermal stabilities by measuring their catalytic performances. The T_{50} and T_{90} over the $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ annealed at 800 °C is 210 and 240 °C, as shown in Figure 8, which is slightly higher than those on the $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ calcined at 500 °C. However, the catalytic activities of the mono-oxides of CeO_2 and SnO_2 are decayed significantly after calcination at 800 °C. The XRD results shown in Supplementary Figure S2 reveal that the crystalline size of CeO_2 on the $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ catalyst calcined at 800 °C was slightly increased from 5.4 to 8.3 nm. Nevertheless, the crystalline sizes of the mono-oxides of CeO_2 and SnO_2 calcined at 800 °C are sharply increased to 37.8 and 25.3 nm, which is the main reason for the decreases in their catalytic performances. The results indicate that the CeO_2 doping with SnO_2 to form a solid solution demonstrates superior thermal stability.

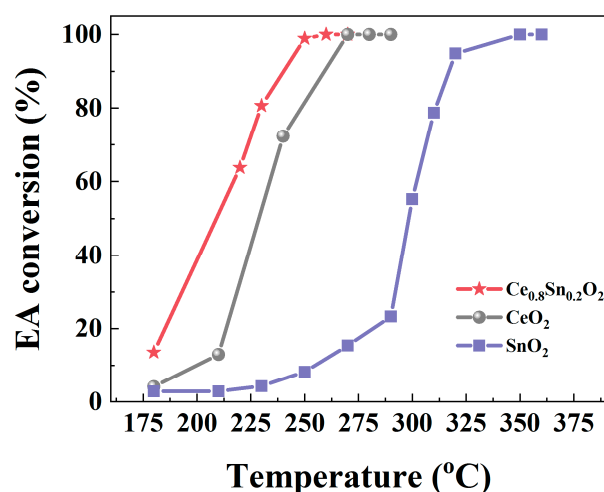


Figure 8. Catalytic activities of the catalysts calcined at 800 °C.

3. Experimental

3.1. Catalyst Preparation

The $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ ($x = 0, 0.2, 0.3, 0.4, 0.5, 0.9, 1$) catalysts were prepared by the combustion method [51,54]. The $\text{Ce}_{0.6}\text{Sn}_{0.4}\text{O}_2$ catalyst was used as an example to clarify the preparation procedure. All the chemicals used in this study were analytic reagents from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. Ceric ammonium nitrate hexahydrate (4.9894 g), stannous oxalate (1.2557 g) and glycine (2.3326 g) were used as precursors of CeO_2 , SnO_2 and fuel, respectively. The above mixture was dissolved in 10 mL of D.I. water and 5 mL HNO_3 to form a clarified solution. Then, the solution was heated at 250 °C, with a stirring rate of 450 r/min, to ignite a violent combustion reaction obtaining a fluffy solid. Finally, the powder was ground and calcined in a tube furnace at 500 °C for 6 h, with a heat rate of 10 °C/min. The catalyst images of different stages are presented in Supplementary Figure S1.

3.2. Catalyst Characterization

XRD experiments were carried out on an instrument of Rigaku Miniflex 600 (Rigaku, Tokyo, Japan) equipped with a Cu target K-ray (40 KV, 15 mA) X-ray source. The diffraction angle (2θ) range was scanned from 20 to 100°, with a step size of 0.02°. The CeO_2 and SnO_2 crystalline sizes were calculated using the Scherrer equation.

SEM characterizations were operated on a ZEISS Sigma 300 (Oberkochen, Germany). TEM images were taken on a FEI Tecnai G2 F20 (Hillsboro, OR, USA). The samples were

dispersed in ethanol and sonicated for 30 min before TEM measurements. Subsequently, the dispersed solutions were dropped on the copper grids and dried in air at room temperature for TEM characterizations.

H₂-TPR experiments were conducted on a VDSorb-91i-BMFC automated chemisorption apparatus (Vodo, QuZhou, China) equipped with a TCD. A total of 50 mg of the catalyst was loaded into a U-shape quartz tube (I.D. = 6 mm). Then, a mixed gas (5% H₂/N₂) with a flow rate of 10 mL/min was introduced to the reactor heating from room temperature to 900 °C, with a heating ramp of 10 °C/min. The H₂ consumption was monitored by a TCD detector after the water and contaminants in the effluent were removed by dried silica.

Specific surface area determinations were conducted on an instrument of Quantachrome NOVA 2200e (Boynton Beach, FL, USA). Prior to testing, the samples were degassed at 200 °C for 6 h. And the adsorption/desorption data of 46 points were acquired at 77 K with a pressure range from 0.05 to 0.25. The specific surface areas were calculated by the Brunner–Emmett–Teller (BET) method.

XPS spectra were obtained on a Thermo Scientific K-Alpha XPS instrument (Hillsboro, OR, USA) with voltage of 12 kW and a filament current of 6 mA. The charge effect was calibrated using a binding energy standard of C 1s (284.8 eV).

3.3. Catalytic Reaction

The catalytic activities of the prepared samples were measured by the reaction of the EA combustion reaction in a fixed-bed reactor produced by Vodo in China. Then, 100 mg of the catalyst was put in the middle of a quartz reactor (D.I.: 6 mm) and fixed by quartz wool between the top and bottom of the reaction tube. A K-type thermocouple inserted into the quartz wool was used to detect the reactant temperature of the inlet, which was controlled by a temperature controller. A total flow rate of 100 mL/min containing 1000 ppm EA and synthetic air (21%O₂/N₂) was adopted with a gas hourly space velocity (GHSV) of 60,000 mL·h^{−1}·g^{−1}. The EA concentration was controlled by the flow rate of synthetic air through the vapor generator of EA at 0 °C. The flow rates of the synthetic air were monitored by mass flow controllers. The organic products were analyzed by a GC equipped with an FID and a column of SE-30. The temperatures for the 50% and 90% conversion of EA that were used to evaluate the catalytic performance of a catalyst were designated as T₅₀ and T₉₀.

4. Conclusions

In this article, the Ce_{1−x}Sn_xO₂ composite catalysts for the catalytic combustion of EA were prepared via the combustion method. The catalytic performances and structures of the Ce_{1−x}Sn_xO₂ are heavily dependent on the X. As the X is within the range of 0 and 0.5, Ce_{1−x}Sn_xO₂ solid solutions are formed and display very good catalytic activities for the EA combustion. And the Ce_{1−x}Sn_xO₂ catalysts with X = 0.2 and 0.3 exhibit the highest catalytic activities with the lowest T₅₀ (190 °C) and T₉₀ (210 °C). Furthermore, the catalytic performance of the Ce_{0.8}Sn_{0.2}O₂ catalyst calcined at high temperature of 800 °C decreases modestly only, showing that the solid solution catalyst has superior thermal stability compared with the pure mono-oxides of CeO₂ and SnO₂. Evidently, there is a synergistic effect between CeO₂ and SnO₂ on the Ce_{1−x}Sn_xO₂ catalysts. The H₂-TPR results show that the reduction abilities of the Ce_{1−x}Sn_xO₂ catalysts are promoted by the incorporation of Sn⁴⁺ into the CeO₂ lattice, attributing to their high catalytic activities. The catalytic activities of Ce_{1−x}Sn_xO₂ catalysts are well correlated to the surface atomic areas of Ce³⁺ and O_α (V_O). The higher the surface atomic areas of Ce³⁺ and O_α (V_O) are, the higher the catalytic activities will be. In conclusion, the Ce_{1−x}Sn_xO₂ solid solution catalysts present excellent catalytic performances and thermal stabilities for the catalytic combustion of EA, which may be potentially used for practical industrial applications for catalytic elimination of VOCs.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13111400/s1>, Figure S1: Figure S1-A: Images of all uncalcined samples after combustion (a: SnO_2 , b: $\text{Ce}_{0.1}\text{Sn}_{0.9}\text{O}_2$, c: $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{O}_2$, d: $\text{Ce}_{0.6}\text{Sn}_{0.4}\text{O}_2$, e: $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$, f: $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$, g: CeO_2). Figure S1-B: Image of all catalysts calcined at 500 °C for 6 h (a: SnO_2 , b: $\text{Ce}_{0.1}\text{Sn}_{0.9}\text{O}_2$, c: $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{O}_2$, d: $\text{Ce}_{0.6}\text{Sn}_{0.4}\text{O}_2$, e: $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$, f: $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$, g: CeO_2). Figure S1-C: Image of all catalysts calcined at 800 °C for 4 h (a: SnO_2 , b: $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$, c: CeO_2). Figure S2: XRD patterns of the catalysts calcined at 800 °C.

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